

Cu-Mn-Co oxides as protective materials in SOFC technology

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1 **Cu-Mn-Co oxides as Protective Materials in SOFC Technology: the Effect of Chemical**
2 **Composition on Mechanochemical Synthesis, Sintering Behaviour, Thermal Expansion and**
3 **Electrical Conductivity**

4

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11 **Abstract**

12 To study the effect of the composition on the physico-chemical properties of mixed Cu-Mn-Co
13 oxides as SOFC interconnects coating materials, different compounds have been obtained through a
14 High Energy Ball Milling (HEBM) process. The mechanochemical treatment produces highly
15 activated multi-phase powders that easily react at intermediate temperature to form the equilibrium
16 products. Thermogravimetric, dilatometric and in-situ high temperature analyses allowed to show
17 that Copper addition promotes cubic spinel stability at low temperature and enhances sintering
18 behaviour.

19 Dilatometric and conductivity analysis carried out on sintered pellets allowed to obtain simple
20 relations between the materials properties and the composition. Coefficient of Thermal Expansion
21 (CTE) and electrical conductivity are increased by Copper doping and high Co:Mn ratios. These
22 findings suggest that the materials characteristics can be opportunely tuned through appropriate
23 composition design, to simultaneously obtain enhanced sintering behaviour, high electrical
24 conductivity and CTE adapted to match the substrate.

25

- 26 Keywords
- 27 Spinel oxides;
- 28 Ball Milling;
- 29 Thermal Expansion;
- 30 Solid Oxide Fuel Cell;
- 31 Interconnect Coating.

32 1. Introduction:

33 Solid Oxide Fuel Cells (SOFCs) represent promising energy conversion devices characterized by
34 high efficiency and virtually absent polluting emissions. To achieve high power required for
35 practical use, the cells are assembled in series to obtain stacks, and a crucial part for the stack
36 design is represented by the cell interconnect. Its role is to separate cathode and anode side of
37 adjacent cells maintaining electrical link and granting structural stability and support. Mechanical
38 compatibility, chemical stability, gas impermeability and high electrical conductivity are needed for
39 proper functionality.

40 In the last decade, research on cell materials permitted to lower operating temperatures below
41 800°C, allowing to design stacks with metallic interconnects characterized by reduced costs and
42 enhanced processability with respect to traditional ceramic parts. Among the metal alloys, Cr-rich
43 ferritic stainless steels possess the Coefficient of Thermal Expansion (CTE) compatibility with
44 SOFC materials, and low cost requirements needed for mass production. In operating environment
45 these alloys undergo however severe corrosion issues, resulting in significant degradation of cell
46 performances. The growth of superficial chromium-rich oxides, besides lowering electrical
47 conductivity, leads in fact to significant chrome volatilization and its subsequent reaction with
48 cathode materials, lowering the cathode active area. Protective coatings that grant electrical
49 conductivity for long term application, inhibiting Cr volatilization, are therefore required[1,2].

50 For this purpose, Mn-Co spinels have been suggested as best candidates, due to their high electrical
51 conductivity and thermal expansion compatibility with ferritic alloys [3]. The composition and
52 thermal history of these compounds influence directly the reticular structure and the chemico-
53 physical properties of the materials [4,5], and several studies have been carried out to further tune
54 mechanical compatibility or electrical properties. The addition of transition metals or reactive
55 elements such as Fe, Ti, Cu, Ni or Y has been evaluated, preparing powders and coating with
56 several methods [6–9]. In particular, it has been observed that the composition affects the thermal
57 expansion behaviour of the compound, and several studies include dilatometric analyses on doped

58 or undoped Mn-Co spinels [3,7,9–15]. While some indications on how chemical composition
59 affects CTE can be deduced (with high Mn, Fe or Ti content decreasing CTE [12] or Ni and Cu
60 increasing CTE [7,9,16]) no clear relation between dopant amount and CTE can be inferred due to
61 significant scattering of the reported results.

62 In our previous work, we have evaluated High Energy Ball Milling (HEBM) as synthesis technique
63 of mixed Mn-Co spinels starting from Mn and Co oxides [17]. HEBM is a mechanochemical
64 technique in which the kinetic energy of colliding balls is transferred to powders trapped against the
65 vial walls. The energy transfer, beside producing comminution and nanostructuration of the
66 powders, promotes interdiffusion of the different chemical elements, atomic rearrangements,
67 nucleation of new phases and other phenomena [18]. Due to the impulsive nature of the energy
68 transfer mechanism, occurring near room temperature, the products are often characterized by
69 metastable phases and highly reactive behaviour [19–21]. In our explorative work we observed that
70 to complete the mechanochemical solid state reaction of Mn and Co oxides, long mechanochemical
71 treatments are needed, but short milling times (i.e. 10 hours) are effective to obtain a highly reactive
72 multi-phase powder. The milled powder can easily form in-situ the equilibrium products during
73 sintering treatments. HEBM is therefore proposed as potential substitute of the high temperature
74 solid state reaction synthesis usually exploited to produce these mixed oxides.

75 In this work, different Mn-Co and Cu-Mn-Co oxide mixtures have been subjected to a short HEBM
76 treatment to prepare spinels characterized by different chemical composition. The compositions
77 were chosen to evaluate how different Mn:Co ratios, possibly in presence of copper, can affect the
78 materials response to the mechanochemical treatment and its properties when exposed to high
79 temperature. High temperature phases evolution, phase stability and sintering behaviour of the
80 treated powder have been studied by means of thermogravimetric analysis, in-situ high temperature
81 X-Ray Diffraction (XRD) and dilatometric measurements. Also the effect of the composition on
82 thermal expansion and electrical conductivity has been evaluated and discussed.

83

84 2. Experimental Procedure

85 The HEBM treatment was carried out using a SPEX8000M mixer mill, cylindrical steel vials (60
86 cm³ volume) and steel balls (10mm diameter) for 10 hours. Stoichiometric amounts of Mn₃O₄
87 (Sigma Aldrich, 97%), Co₃O₄ (Sigma Aldrich, 99%) and CuO (Carlo Erba, 99%) were mixed in
88 order to obtain the samples with composition reported in Table 1. A powder to balls weight ratio of
89 1:10 was used for the experiments; vials were loaded with 8g of powders and sealed under argon
90 atmosphere.

91

92 *Table 1: Sample nomenclature and nominal composition:*

Sample name	Metal ratio			Corresponding composition
	Mn	Co	Cu	
MnCo2	0.33	0.67		MnCo ₂ O ₄
Mn1.25Co1.75	0.42	0.58		Mn _{1.25} Co _{1.75} O ₄
Mn1.5Co1.5	0.50	0.50		Mn _{1.5} Co _{1.5} O ₄
Mn1.33Co1.17Cu0.5	0.44	0.39	0.17	Mn _{1.33} Co _{1.17} Cu _{0.5} O ₄
Mn1.58Co0.93Cu0.5	0.52	0.31	0.17	Mn _{1.57} Co _{0.93} Cu _{0.5} O ₄
Mn2.05Co0.45Cu0.5	0.68	0.15	0.17	Mn _{2.05} Co _{0.45} Cu _{0.5} O ₄

93

94 A 120° angular dispersion X-ray diffractometer (XRD3000 from Italstructure, curved PSD detector
95 from INEL), equipped with Fe K_{α1} radiation source, was used to perform X-Ray diffraction analysis
96 (XRD). Phase identification was performed on collected patterns using the PDF-2 database[22] as
97 reference data. Lorentzian fitting of selected reflections allowed to evaluate cell parameters and to
98 calculate accordingly theoretical densities, considering nominal compositions of the samples. In situ
99 high temperature measurements were performed installing a heating reactive chamber (Anton Paar

Gmbh, Graz, Austria). The measurements were carried out in air, at heating and cooling rates of 10°C/min, 300 s of thermal equilibrium time before the measurements and 300 s of acquisition time.

Scanning Electron Microscopy (SEM) analyses were carried out on a Hitachi TM3030Plus SEM equipped with EDX energy-dispersive X-ray (EDX) microanalysis.

N₂ adsorption at 77K technique (Quantachrome Autosorb-iQ) was exploited to evaluate mean particle size. Specific Surface Area (SSA) was calculated applying the BET method[23]. Average particle size was calculated assuming spherical particle shape.

Thermogravimetric analyses were carried out in air using a Pyris Diamond TG/DTA (Perkin Elmer), heating the samples up to 1200°C at 5°C/min, followed by 60 minutes of high temperature dwell time and cooling to room temperature at 5°C/min.

Dilatometric measurements were carried out using a push-rod dilatometer (DIL 402 C, NETZSCH). To evaluate sintering behaviour, consolidated pellets of about 6mm diameter were obtained by uniaxial cold pressing (3.5 T/cm²). The experiments were carried out heating at 5°C/min scan rate up to 1200°C. To measure thermal expansion, experiments were carried out on pellets of about 6mm diameter and 2.5mm height sintered as described later in the text. The measurements were carried out with a heating rate of 10°C/min. Average CTE was calculated between room temperature and 800°C as: $CTE = \frac{1}{L_0} \frac{\Delta L}{\Delta T}$, where L_0 represents the initial length and ΔL the length change occurring in the ΔT temperature range.

Electrical conductivity was estimated by applying the Van der Pauw method [24] on pellets of about 10mm diameter, obtained by uniaxial cold pressing (3.5 T/cm²) and successive sintering (see below for experimental details). The 500-800°C temperature range was investigated, using a PAR273A potentiostat coupled to a HP 3457A multimeter. Activation energy E_a was calculated from the Arrhenius plot obtained using the formula: $\sigma = \frac{\sigma_0}{T} e^{-\frac{E_a}{kT}}$, with σ electrical conductivity, T temperature, σ_0 pre-exponential factor, E_a activation energy and k Boltzmann's constant.

125 3. Results and discussion

126 3.1. Powder characterization

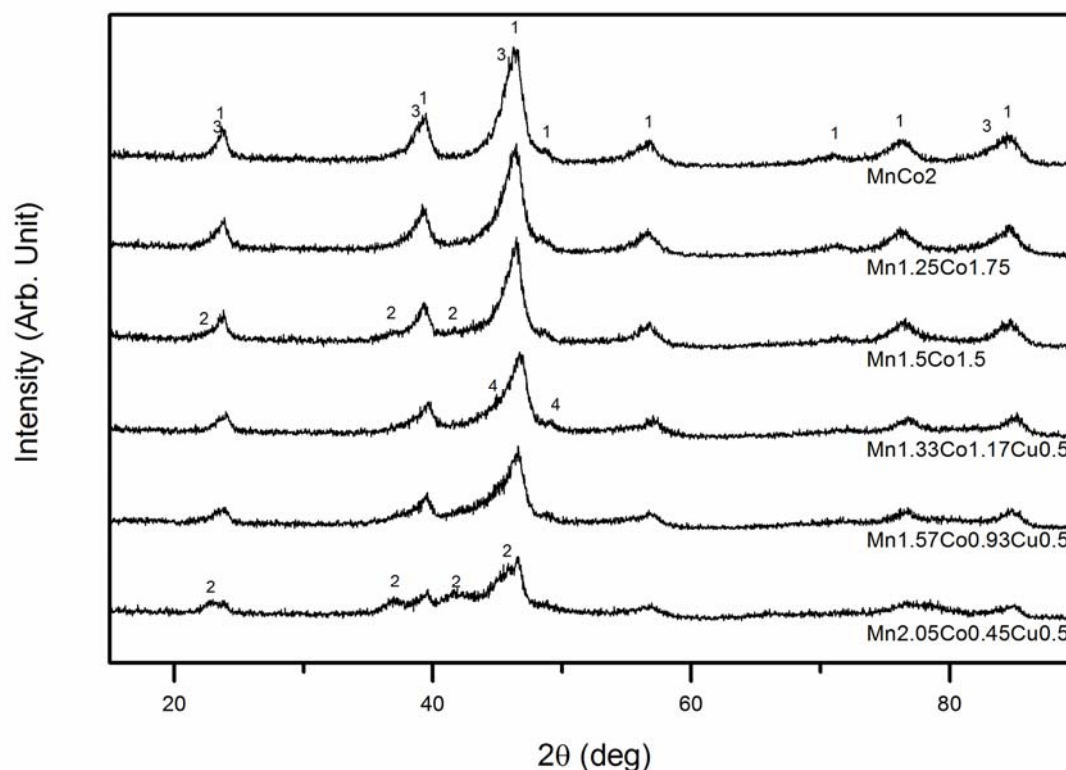
127 The mechanochemical treatment produces fine black powders. After the milling treatments, EDX
128 analyses have been successfully carried out to exclude the presence of iron and chromium that
129 could highlight chemical contamination from the milling equipment. In Fig. 1 are reported the XRD
130 patterns of the samples after 10 hours of milling. Significant peak broadening can be observed due
131 to nanostructuration of diffractive domains and lattice defectivity induced by the HEBM treatment.
132 The three Mn-Co samples evidence the residual presence of the Co_3O_4 precursor phase (JCPDS
133 card n. 42-1467). The observed asymmetry towards lower angles can be related to the nucleation of
134 a mixed MnCo_2O_4 phase (JCPDS card n. 23-1237). Only the $\text{Mn}_{1.5}\text{Co}_{1.5}$ sample shows signals
135 related to the Mn_3O_4 precursor phase (JCPDS card n. 24-0734).

136 Cu-containing samples show similar peak broadening. The $\text{Mn}_{1.33}\text{Co}_{1.17}\text{Cu}_{0.5}$ pattern exhibits
137 mainly reflections compatible with the Co_3O_4 phase, with the already observed asymmetry towards
138 lower angles. Small broadened peaks at $2\theta \cong 45$ and $2\theta \cong 49$ degrees are ascribable to the presence of
139 CuO phase (JCPDS card n. 48-1548). Raising Mn content, reflections related to Mn_3O_4 become
140 evident, similarly to what was observed for the Mn-Co samples.

141 The higher stability exhibited by the cobalt precursor phase in comparison with to the Mn and Cu
142 oxides with respect the mechanochemical action is clearly evident from these results. The
143 $\text{Mn}_{1.5}\text{Co}_{1.5}$ sample, composed by similar Co and Mn amounts, is characterized by Mn_3O_4
144 reflections scarcely visible with respect to the cubic Co_3O_4 phase peaks. Regarding copper oxide, it
145 can be clearly observed from the pattern related to the $\text{Mn}_{2.05}\text{Co}_{0.45}\text{Cu}_{0.5}$ sample, that also the
146 CuO phase gets easily destructured during the milling, the CuO peaks being significantly lower and
147 broader with respect to those of cobalt oxide. The observed phenomena can be ascribed to the
148 difference in hardness of the materials, with Co spinel characterized by significantly higher
149 hardness with respect to Hausmannite (Mohs hardness: 5.5) [25] and Tenorite (Mohs hardness:

150 3.5-4). The successive destructure of the crystalline phases easily promotes interdiffusion of Mn
 151 and Cu atoms in the Co precursors phase or in the nucleating mixed spinel lattice.

152



153

154 *Fig. 1. X-ray powder diffraction patterns of the different samples after 10h of milling; 1) Co_3O_4 2) Mn_3O_4)*
 155 *MnCo_2O_4 4) CuO reflections.*

156

157 In Table 2 BET specific surface area and calculated mean particle size are reported. All the samples
 158 exhibit comparable values, with Copper-containing powders characterized by the lower BET area,
 159 suggesting that Copper addition promotes higher aggregation degree. Mean particle size ranges
 160 between 170 and 330nm.

161

162 *Table 2: BET surface area and BET particle size for the 10h HEBM powders:*

Sample	BET	\bar{d}
--------	-----	-----------

	(m ² /g)	(nm)
MnCo2	6.2±0.3	176±9
Mn1.25Co1.75	5.7±0.3	195±10
Mn1.5Co1.5	4.5±0.2	255±12
Mn1.33Co1.17Cu0.5	4.2±0.2	265±13
Mn1.57Co0.93Cu0.5	3.5±0.2	325±15
Mn2.05Co0.45Cu0.5	4.1±0.2	293±13

$$*l = \frac{6}{A_{BET} \cdot \rho}$$

163

164 In order to evaluate how the different Mn:Co ratios and the Cu addition influence the high
165 temperature properties of the samples, the milled powders were subjected to thermogravimetric
166 analysis. In Fig. 2 thermogravimetric analysis curves are reported. All samples show a weight loss
167 step ascribable to the departure of adsorbed humidity. In the 200-500°C temperature range, a
168 gradual weight increase can be observed for all compositions. The effectiveness of
169 mechanochemical activation can be recognized from this phenomenon: the HEBM treatment
170 promotes in fact high degree of interdiffusion of the starting oxides, and being carried out in Ar
171 atmosphere it is likely to create anion defective lattices. The highly defective and nanostructured
172 powders will easily react at low temperature with oxygen, most likely leading to the oxidation of
173 Mn to higher oxidation states. The low cation mobility at low temperature does not however allow
174 major lattice rearrangement, producing metastable non-stoichiometric compounds. Similar
175 metastable mixed valence spinels have been already observed for transition metal oxide systems,
176 although prepared by other routes, and their formation was related to a high reactivity associated
177 with highly nanostructured compounds [26].

178 Raising the temperature, in the 500-700°C temperature range, the Mn-Co and Mn1.33Co1.17Cu0.5
179 samples show a similar gradual weight loss, reaching a plateau for higher temperatures. In this
180 temperature range, for the Mn-Co samples the reaction between the activated precursors is expected

181 [17]. The release of the extra oxygen content acquired during the previous weight acquisition step,
182 followed by an interval of weight stability, is compatible therefore with the reorganization of the
183 metastable oxidized lattices to form high temperature stable phases.

184 The Mn richest samples, i.e. $\text{Mn}_{1.57}\text{Co}_{0.93}\text{Cu}_{0.5}$ and $\text{Mn}_{2.05}\text{Co}_{0.45}\text{Cu}_{0.5}$, undergo instead a
185 further weight acquisition step before exhibiting weight loss. In our previous work we had observed
186 how the presence of Mn-rich unreacted spinels could lead to the oxidation of Mn_3O_4 to Mn_2O_3
187 during heating, and it is likely to ascribe this weight gain to a similar phenomenon. Raising further
188 the temperature, the oxidized compound reacts with the existing spinels, resulting in weight loss and
189 formation of spinel phases. The behaviour of the Cu-doped samples will be further investigated in
190 the next section by means of the outcome of in-situ high temperature XRD analysis.

191 Further heating over 1000°C leads to an additional weight loss phenomenon for all samples except
192 $\text{Mn}_{1.5}\text{Co}_{1.5}$. Regarding Mn-Co samples, it is known that at high temperature, a multi-phase
193 boundary between spinels and reduced Me^{II} oxide phases exists for Co-Mn oxide mixtures [4], with
194 equilibrium temperature increasing with Mn content. The absence of the weight loss phenomena for
195 the sample $\text{Mn}_{1.5}\text{Co}_{1.5}$ indicates for this composition a phase boundary temperature beyond
196 1200°C . In the case of Cu addition, a similar behaviour can be supposed, with a dual phase region
197 also for the mixed Cu-Mn-Co oxides. Unlike Mn-Co samples, the weight loss is observed for all the
198 compositions. Considering that the $\text{Mn}_{2.05}\text{Co}_{0.45}\text{Cu}_{0.5}$ sample is characterized by an approximate
199 4:1 Mn:Co ratio, it is evident that copper lowers significantly the dual phase region boundary
200 temperature.

201 During cooling, the high temperature weight loss phenomenon is recovered for all samples, and no
202 significative weight change phenomena can be observed.

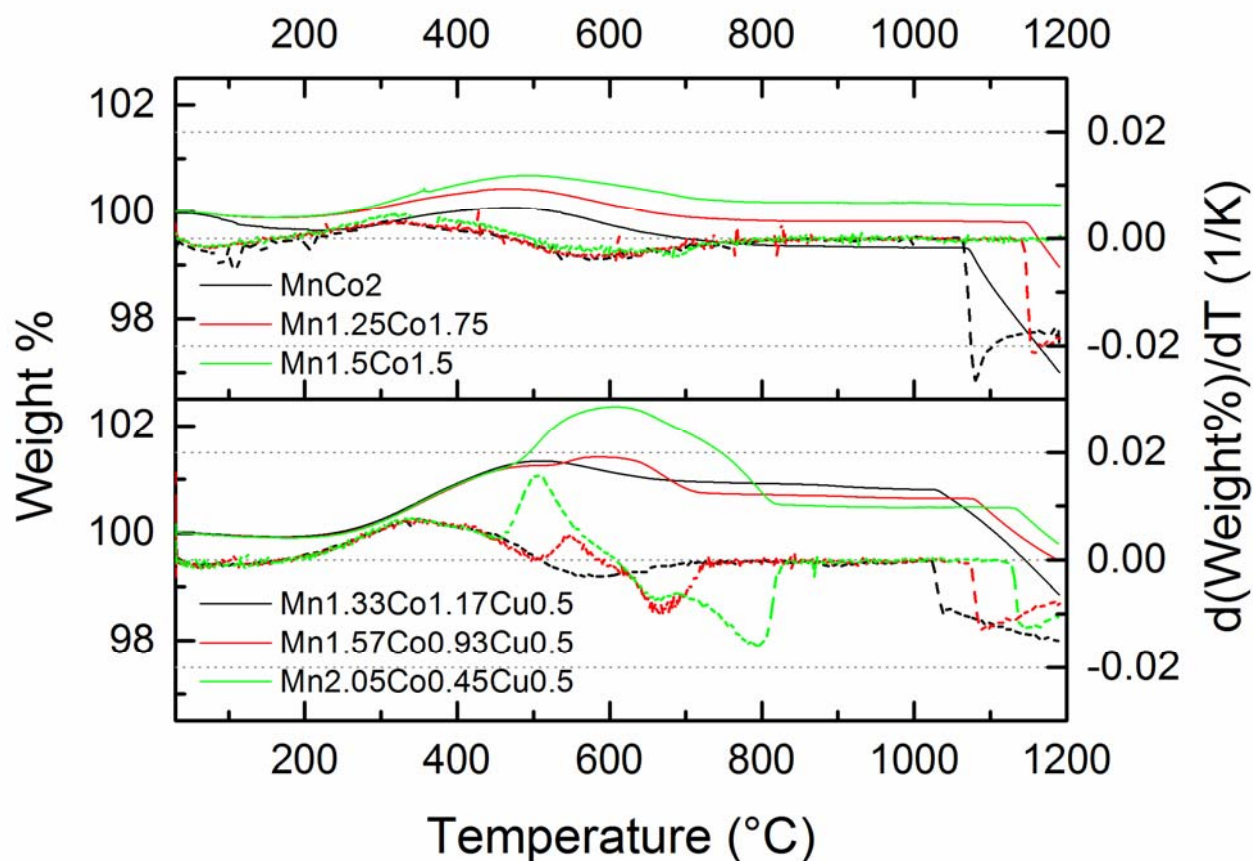


Fig. 2. Thermogravimetric curves as a function of temperature for the different samples; solid lines represent weight% change, dotted lines the derivative.

To further investigate the behaviour of the Cu doped samples upon heating, in situ diffraction analyses were carried out on the ball-milled powders. High temperature patterns are reported in Fig. 3.

Starting from the $\text{Mn}_{1.33}\text{Co}_{1.17}\text{Cu}_{0.5}$ sample, the pattern collected at 400°C is substantially similar to that acquired at room temperature, confirming that the oxidation phenomena observed with TGA measurements do not involve reactions or significant nucleation of new phases. The reaction between the activated precursors is instead evident at 500°C , where the nucleation of a cubic spinel phase occurs. Heating further, the reaction between the remaining precursors carries on, forming a single cubic spinel phase. The weight loss observed in the $500\text{--}700^\circ\text{C}$ by thermogravimetric measurements can be associated therefore to the rearrangement of the metastable

oxidized lattice, resulting in the nucleation of the high temperature spinel. During cooling, no structural changes are evident, showing that the examined composition is characterized by a single phase nature in the ambient – 800°C temperature range.

The initial evolution of Mn_{1.57}Co_{0.93}Cu_{0.5} sample is similar, with the nucleation of a cubic spinel phase in the 400°C-500°C interval. At 600°C reflections ascribable to the Mn₂O₃ phase (JCPDS card n. 24-0508) are visible, explaining the thermogravimetric weight gain occurring in the 600-700°C range. The growth of the spinel phase carries along with it the increase of peaks related to this Mn-rich phase up to 700°C. Between 700°C and 800°C the rising spinel phase and Mn₂O₃ react, and the pattern collected at 800°C is ascribable to the presence of a single spinel phase. During cooling, this phase is stable down to 500°C. At 400°C, reflections ascribable to a tetragonal spinel phase similar to Mn₂CoO₄ (JCPDS 48-1548) appear, indicating the decomposition of the high temperature cubic phase with the formation of a dual phase compound.

Regarding the Mn_{2.05}Co_{0.45}Cu_{0.5} sample, coherently with thermogravimetric results, nucleation of large amounts of the oxidized Mn₂O₃ phase occur already at 500°C, along with the formation of a cubic spinel phase. The transformation of Mn₃O₄ and Co₃O₄ precursor phases occurs between 500°C and 700°C, where only Mn₂O₃ and the spinel phase are visible. Raising the temperature, Mn₂O₃ and the spinel phase react, and at 800°C the spinel phase formation is almost complete. Similarly to what was observed for the Mn_{1.57}Co_{0.93}Cu_{0.5} sample, during cooling the segregation of a tetragonal spinel phase is observed at a temperature value between 700°C and 600°C.

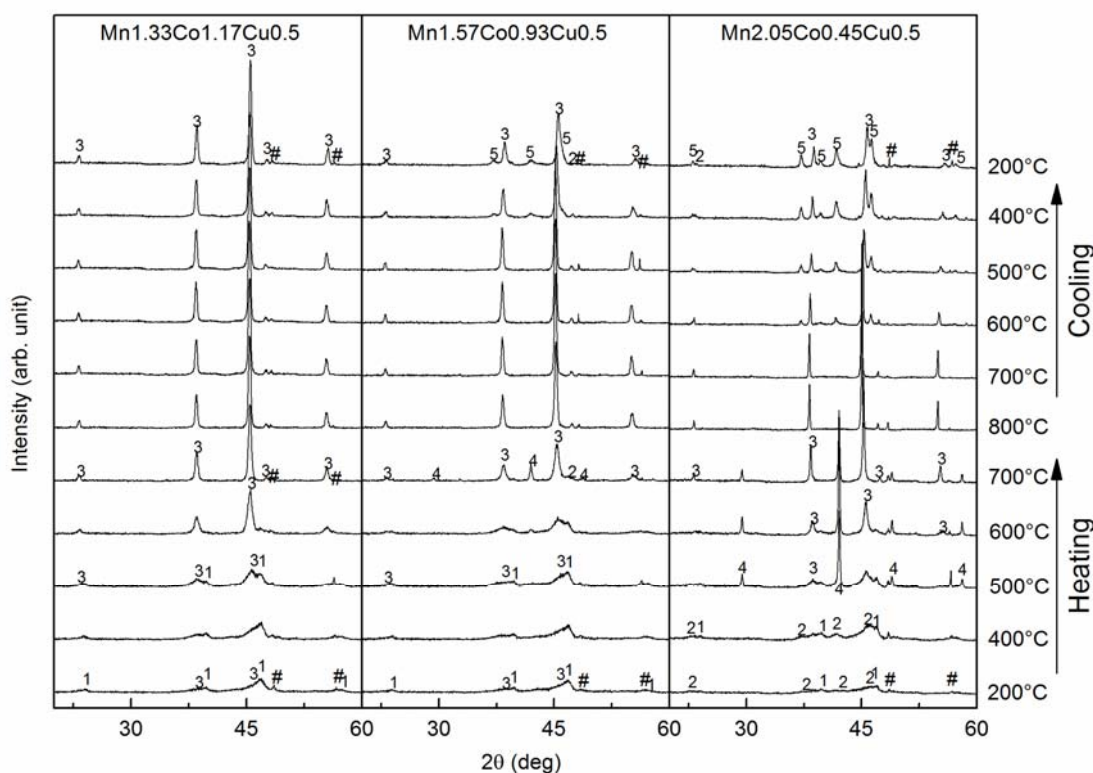


Fig. 3: In situ X-ray diffraction patterns of a) $\text{Mn}_{1.33}\text{Co}_{1.17}\text{Cu}_{0.5}$, b) $\text{Mn}_{1.57}\text{Co}_{0.93}\text{Cu}_{0.5}$ and c) $\text{Mn}_{2.05}\text{Co}_{0.45}\text{Cu}_{0.5}$ samples milled for 10 hours collected at different temperatures (heating rate = $10^\circ\text{C}/\text{min}$). Reflections ascribable to 1) Co_3O_4 2) Mn_3O_4 3) MnCo_2O_4 4) Mn_2O_3 5) Tetragonal mixed spinel phase and #) sample holder are indicated.

The evaluation of sintering behaviour was carried out on consolidated pellets prepared by uniaxial cold pressing. To compare sintering properties meaningfully, and ascribe differences to chemistry rather than to morphology of the powders, comparable pellet density is crucial. The geometric green densities are reported in Table 3: similar values are obtained for all the different samples, as expected from the processing of morphologically similar powders. The consolidated pellets were subjected to dilatometric measurements between room temperature and 1200°C , with a $5^\circ\text{C}/\text{min}$ heating rate. Shrinkage curves are reported in Fig. 4. No significant differences can be observed between Mn-Co samples, with sintering temperatures of about $1040\text{--}1060^\circ\text{C}$ and maximum densification rates at approximately 1150°C . Copper addition greatly enhances sintering behaviour: sintering temperatures are lowered to about 910°C , 870°C and 830°C respectively for

253 Mn_{1.33}Co_{1.17}Cu_{0.5}, Mn_{1.57}Co_{0.93}Cu_{0.5} and Mn_{2.05}Co_{0.45}Cu_{0.5}, and the shrinkage extent is
254 greatly increased with respect to Mn-Co samples. High temperature dilatation phenomena are
255 however visible in Mn_{1.33}Co_{1.17}Cu_{0.5} and Mn_{1.57}Co_{0.93}Cu_{0.5} curves. To further investigate
256 this phenomenon, a pellet obtained by pressing Mn_{1.33}Co_{1.17}Cu_{0.5} powder was heated in furnace
257 at 1200°C for 10 minutes and slowly cooled. The SEM image is reported in Fig. 5a. Significant
258 grain growth and inter-grain porosity can be observed, as well as the presence of an irregular and
259 corrugated Cu-rich phase. The observation of the samples clearly suggests a liquid phase sintering
260 at high temperature, most likely due to segregation and melting of the Cu-rich phase, that could
261 result in swelling phenomena [27]. The contemporary release of oxygen gas, as observed by
262 thermogravimetric analysis, when occurring in a highly packed structure could furthermore enhance
263 the expansion phenomena.

264 XRD analysis of the pellets after dilatometric measurements demonstrated in most cases secondary
265 phases in addition to the spinel. Differently from TGA measurements, the pelletized materials did
266 not recover the oxygen loss properly during cooling, probably due to higher packing of particles,
267 high crystal growth and subsequent reduced oxygen diffusion kinetics.

268

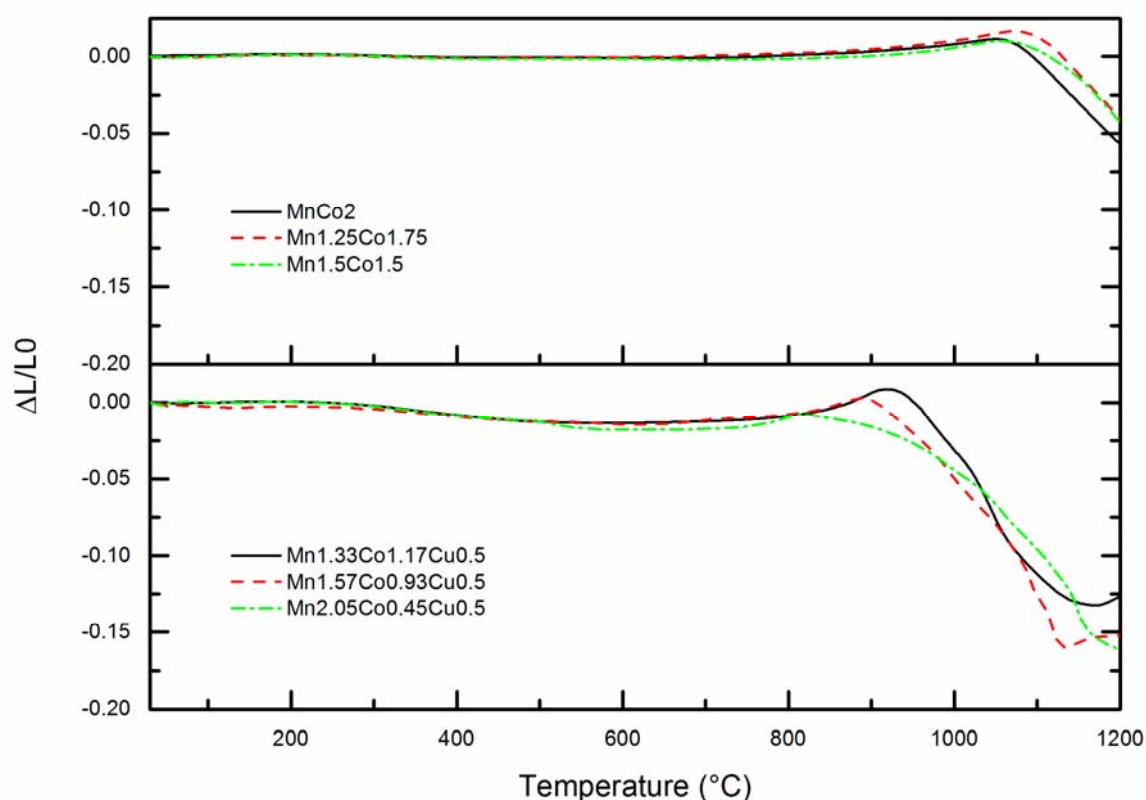
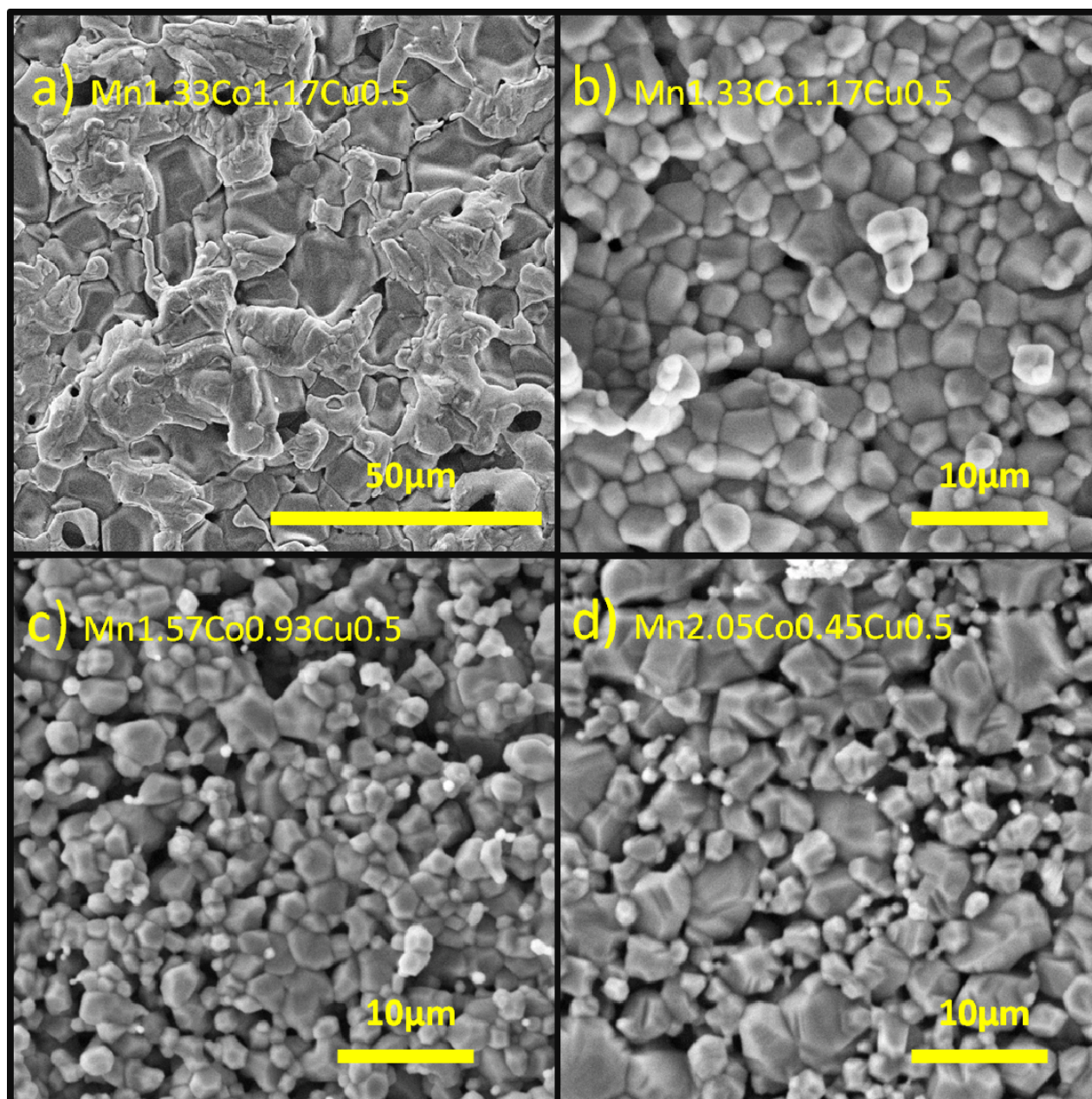


Fig. 4. Dilatometric curves as a function of temperature of the different samples.

The undesired phase segregation upon sintering at high temperature is an issue to precisely determine CTE and electrical properties of the material. Therefore, the sintering treatment of the pellets needed for dilatometry and Van der Pauw experiments was tailored. In the case of Mn-Co samples, it was not possible to reduce the temperature to avoid secondary phase formation, but a second dwell at lower temperature (i.e. 800°C) was successfully introduced to facilitate the spinel recovery. For MnCo₂ sample a further annealing (16h at 1000°C) was required to achieve single phase pellets, as observed for similar samples prepared with other synthesis routes [8]. For Mn-Co-Cu samples instead, the lower sintering temperature setup, as observed in dilatometric measurements, allowed to reduce the thermal treatment to 1000°C, avoiding segregation of Cu-rich phases and still obtaining sufficiently dense pellets. In Fig. 5b-d SEM images of the Mn_{1.33}Co_{1.17}Cu_{0.5}, Mn_{1.57}Co_{0.93}Cu_{0.5} and Mn_{2.05}Co_{0.45}Cu_{0.5} samples after sintering at 1000°C are reported. A homogeneous morphology can be observed, characterized by significantly

284 lower crystal growth with respect to the 1200°C thermal treatment. In Table 3 a summary of the
285 performed thermal treatments and the geometrical density measured after sintering is reported. It
286 can be noted that Cu addition leads to densities comparable to Mn-Co samples even with a 200K
287 reduction in sintering temperature.
288



289

290 *Fig. 5: SEM images of samples heat treated at a) 1200°C and b,c,d) 1000°C (see text for details).*

291

Sample	Green density %	Sintering treatment	Sintered density %
MnCo2	66±1	4 h @1200°C + 4 h @800°C 16h @ 1000°C post sintering	93±1
Mn1.25Co1.75	67±1	4 h @1200°C + 4 h @800°C	93±1
Mn1.5Co1.5	67±1		95±2
Mn1.33Co1.17Cu0.5	65±1		97±1
Mn1.57Co0.93Cu0.5	64±1	4 h @1000°C + 4 h @800°C	97±2
Mn2.05Co0.45Cu0.5	65±1		97±2

293

294 In Fig. 6 X-Ray diffraction patterns of the sintered samples are reported. MnCo2 and
295 Mn1.25Co1.75 show a pattern ascribable to a single cubic phase, with small shifts due to different
296 Mn:Co ratio, while Mn1.5Co1.5 exhibits a mixture of a tetragonal and cubic spinels. These results
297 are in agreement with the Mn-Co oxides phase diagram at room temperature. A single cubic phase
298 is stable for high Co content (Co:Mn>1.3), a single tetragonal phase is obtained for high Mn content
299 (Co:Mn<0.5), while for intermediate compositions, depending on the synthesis and cooling method,
300 a mixture of the two phases or a single metastable tetragonal phase is observed[4,5]. Regarding Cu-
301 Mn-Co samples, as observed by HT-XRD, Mn1.33Co1.17Cu0.5 is characterized by a single cubic
302 phase, while raising Mn content peaks ascribable to a tetragonal spinel phase appear. Differently
303 from Mn-Co composition, where Mn rich spinels exhibit a single tetragonal phase, copper addition
304 enhances the cubic phase stability region, as evident by the phase composition of the
305 Mn2.05Co0.45Cu0.5 sample, characterized by a mixture of cubic and tetragonal phases.

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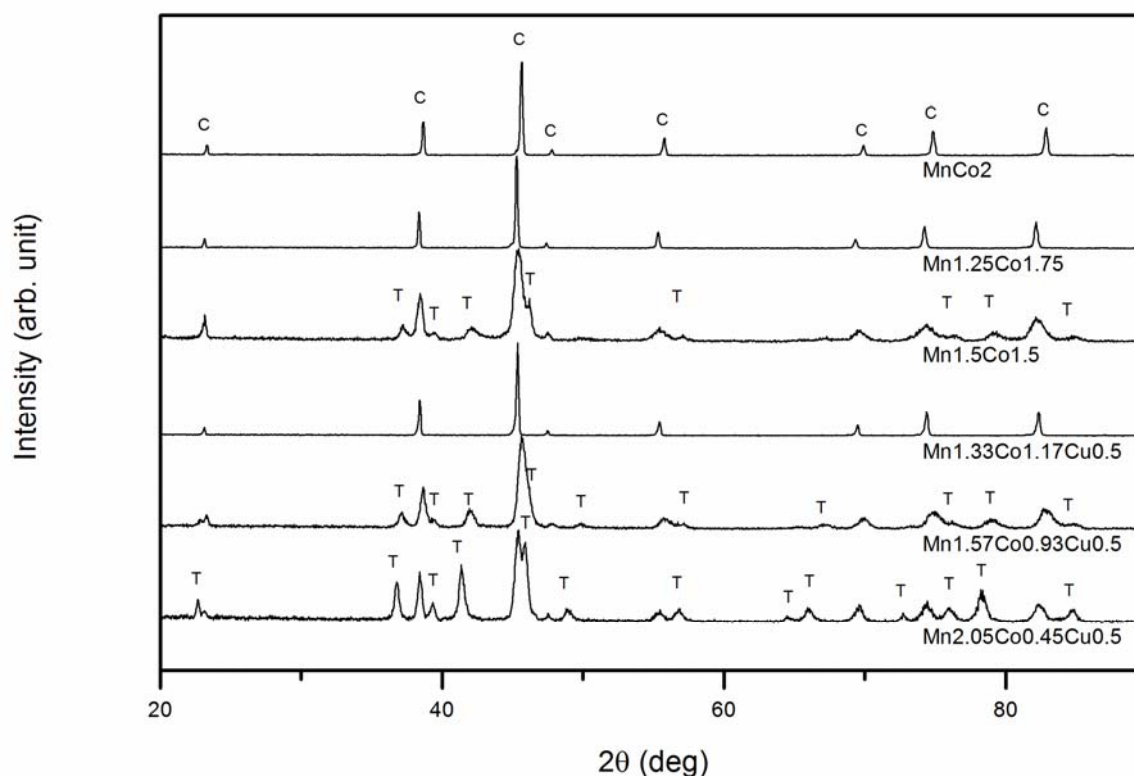


Fig. 6. X-ray powder diffraction patterns of the samples after sintering treatment; C specify reflections ascribable to a cubic spinel phase, T to a tetragonal spinel phase.

3.2. Thermal expansion

To evaluate the CTE of the different compositions, the sintered pellets were subjected to dilatometric analyses, and the obtained curves are reported in Fig. 7. Regarding Mn-Co samples, it can be observed that higher Co content induces higher expansion. MnCo₂ and Mn_{1.25}Co_{1.75} samples, characterized by a single phase in the whole examined temperature range, show a corresponding linear behaviour. Mn_{1.5}Co_{1.5} curve shows instead a discontinuity in the 500-600°C temperature range, ascribable to the dual phase – single phase transition. Regarding copper addition, a similar behaviour can be observed: the dual-phase samples (those richest in Mn) exhibit a discontinuity in the 450-600°C temperature range and in the 600-750°C for the Mn_{1.57}Co_{0.93}Cu_{0.5} and Mn_{2.05}Co_{0.45}Cu_{0.5} samples respectively, most likely related to the dual-single phase transition occurring in these temperature intervals.

322 Average CTE values have been calculated between room temperature and 800°C, and are reported
 323 in Table 4. Among the considered composition, Mn_{1.57}Co_{0.93}Cu_{0.5} and Mn_{1.25}Co_{1.75} exhibit
 324 the highest compatibility with thermal expansion of ferritic stainless steels ($11-13 \cdot 10^{-6} \text{ K}^{-1}$ [28]). To
 325 evaluate how the different Mn:Co ratio and Cu addition influence CTE, in Fig. 8 are reported the
 326 CTE values at 800°C versus the cobalt content for the different samples. Regarding Mn-Co
 327 composition, a clear linear trend can be observed between the composition and CTE values. Also
 328 for Cu doped samples an analogue behaviour can be observed when changing Mn:Co ratio, and Cu
 329 addition does not affect significantly this trend but rather induces a shift of the curve toward higher
 330 CTEs.

331 The observed behaviour can be ascribed to the chemical differences between the samples
 332 considering lattice sites occupations and atoms valence. In particular, thermal expansion of mixed
 333 metal spinels can be related to the composition principally via the occupation of octahedral sites
 334 [29], where compounds characterized by high valence differences possess higher CTE.

335 Mn-Co spinels are characterized by a preferential occupation of tetrahedral sites by Co^{II} atoms. Co^{II},
 336 Co^{III}, Mn^{III} and Mn^{IV} occupy octahedral sites, with Co^{II} and Mn^{IV} amounts related to electro-
 337 neutrality constraints [30]. In the $1:1 \leq \text{Co:Mn} \leq 2:1$ compositional range, the increase of Co promotes
 338 an increase of Co^{II}, Co^{III} and Mn^{IV} species at the expense of Mn^{III} atoms[31]. Increasing Co content
 339 in this composition range will cause therefore higher inhomogeneity, theoretically raising CTE, in
 340 agreement with our results.

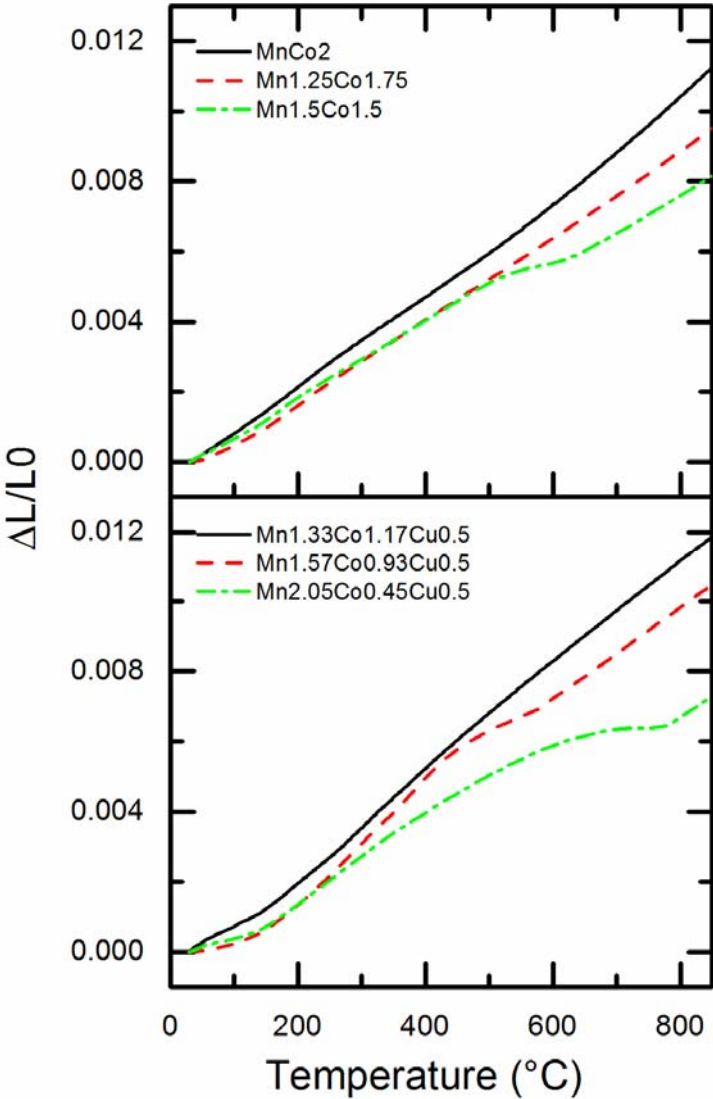
341 In mixed Cu-Co-Mn compounds instead, Cu^I/Cu^{II} species tend to occupy tetrahedral sites
 342 preferentially over Co^{II} atoms, leading to an enrichment of Co^{II}/Co^{III} pairs in octahedral sites [32].
 343 Furthermore, the presence of Cu^I atoms promotes Mn^{III} oxidation to Mn^{IV} to maintain charge
 344 neutrality. Valence differences are therefore increased with copper doping, enhancing CTE.

345

346 Table 4. Thermal expansion coefficient at 800°C measured for the different samples:

Sample	CTE @800°C ($\cdot 10^{-6} \text{ K}^{-1}$)
MnCo2	13.5 \pm 0.1
Mn1.25Co1.75	11.5 \pm 0.1
Mn1.5Co1.5	9.7 \pm 0.1
Mn1.33Co1.17Cu0.5	14.5 \pm 0.1
Mn1.57Co0.93Cu0.5	12.7 \pm 0.1
Mn2.05Co0.45Cu0.5	8.5 \pm 0.1

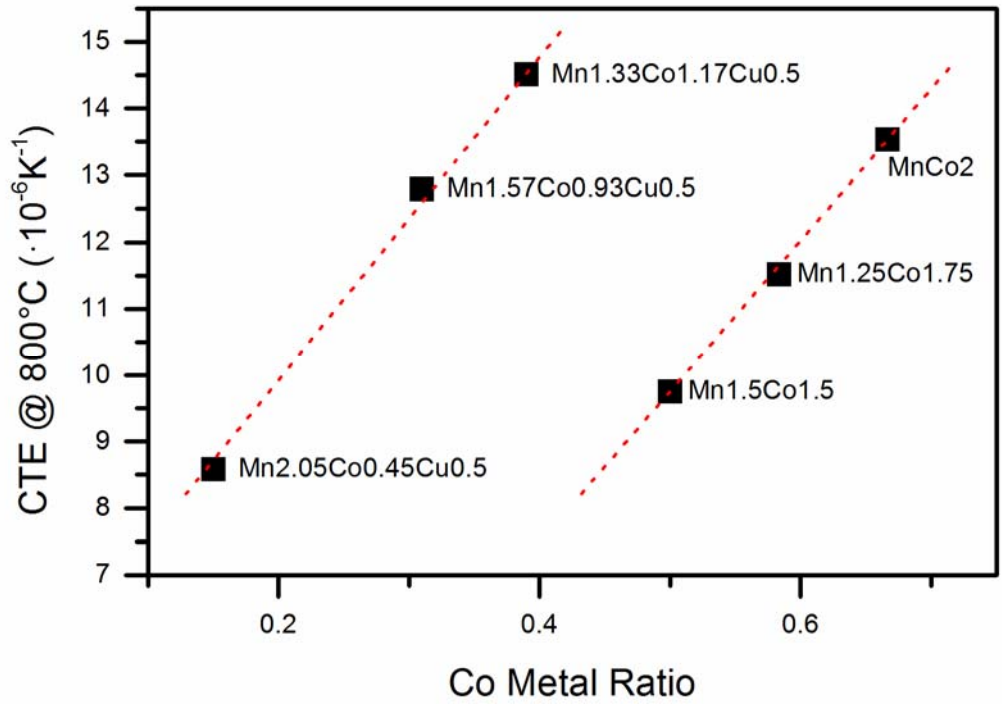
347



348

349 Fig. 7. Thermal expansion curves of the sintered samples.

350



351

352 *Fig. 8. Coefficient of thermal expansion calculated at 800°C as a function of the sample composition.*

353

354 3.3. Electrical conductivity

355 Electrical conductivity measurement was carried out by means of the Van der Pauw method in the
356 temperature range 500-800°C. In Fig. 9 are reported Arrhenius plots.

357 MnCo₂, Mn_{1.25}Co_{1.75} and Mn_{1.33}Co_{1.17}Cu_{0.5} samples exhibit a linear behaviour through all the
358 examined range, as expected by their single phase nature. On the contrary, samples characterized
359 by dual to single phase transitions show slope changes in their linear trend, at temperatures coherent
360 with the discontinuities observed during dilatometric measurements. From the single-phase region
361 of the Arrhenius plots, the activation energies were calculated and are reported in Table 5. Mn-Co
362 samples exhibit comparable values of about 0.5eV, while Cu addition lowers significantly in all
363 cases the activation energy to about 0.3eV.

364 To better evaluate how Mn:Co ratio and Cu addition affect electrical properties, in Fig. 10 are
365 reported conductivity values measured at 800°C versus cobalt content. The MnCo₂ sample is

characterized by a conductivity value of about 80S/cm, and a decreasing trend can be observed increasing Mn content. A similar decrease in conductivity with Mn content can be observed for the Cu doped samples as well. On the other hand, Cu addition increases electrical conductivity, with the Mn_{1.33}Co_{1.17}Cu_{0.5} sample characterized by a conductivity value of about 125S/cm.

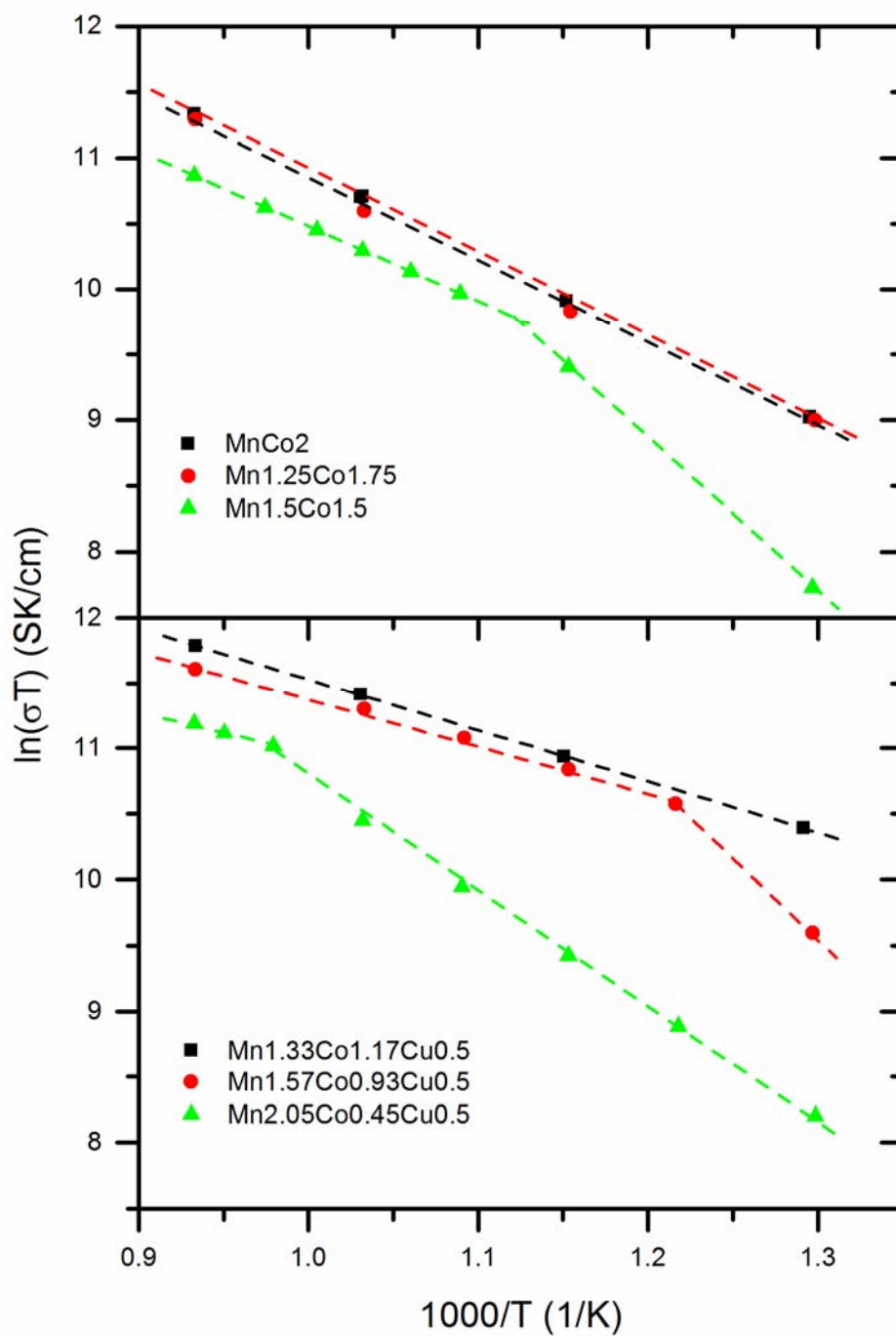
In such spinel systems, the conductivity behaviour is usually explained with a small polaron hopping mechanism between mixed valence elements on octahedral sites, and in Mn-Co oxides it is usually related to Co^{II}/Co^{III} and Mn^{III}/Mn^{IV} pairs [3,30,31]. The Co^{II}/Co^{III} and Mn^{III}/Mn^{IV} concentration ratio affects therefore conductivity properties, Co^{III} and Mn^{III} being the most common species in octahedral sites. The observed trend for Mn-Co samples is in agreement with previous findings, and is related to the maximum concentration of Co^{II} and Mn^{IV} species for compositions with Mn:Co≈2:1 [31]. The similar increasing trend here observed for the Cu-doped samples suggests that similar phenomena can be accounted for also in Cu-Mn-Co samples. The significant increase of conductivity in Cu samples with respect to Mn-Co compounds can be instead due to multiple mechanisms. Copper addition in mixed Mn-Co spinels occurs with preferential occupation of tetrahedral sites of the spinel lattice by Cu^I and Cu^{II} species, that promotes Mn^{III} oxidation to Mn^{IV} to maintain charge neutrality. As a consequence, Cu introduction increases active pairs concentration and therefore electrical conductivity [32]. Tetrahedral Cu ions could furthermore contribute indirectly to electrical conductivity, through mediation of charge transfer mechanisms between near but not adjacent Mn atoms, as observed in Ni-Cu manganite spinels [33].

385

386 *Table 5. Activation energy calculated from the Arrhenius plot of 10 hours milled samples:*

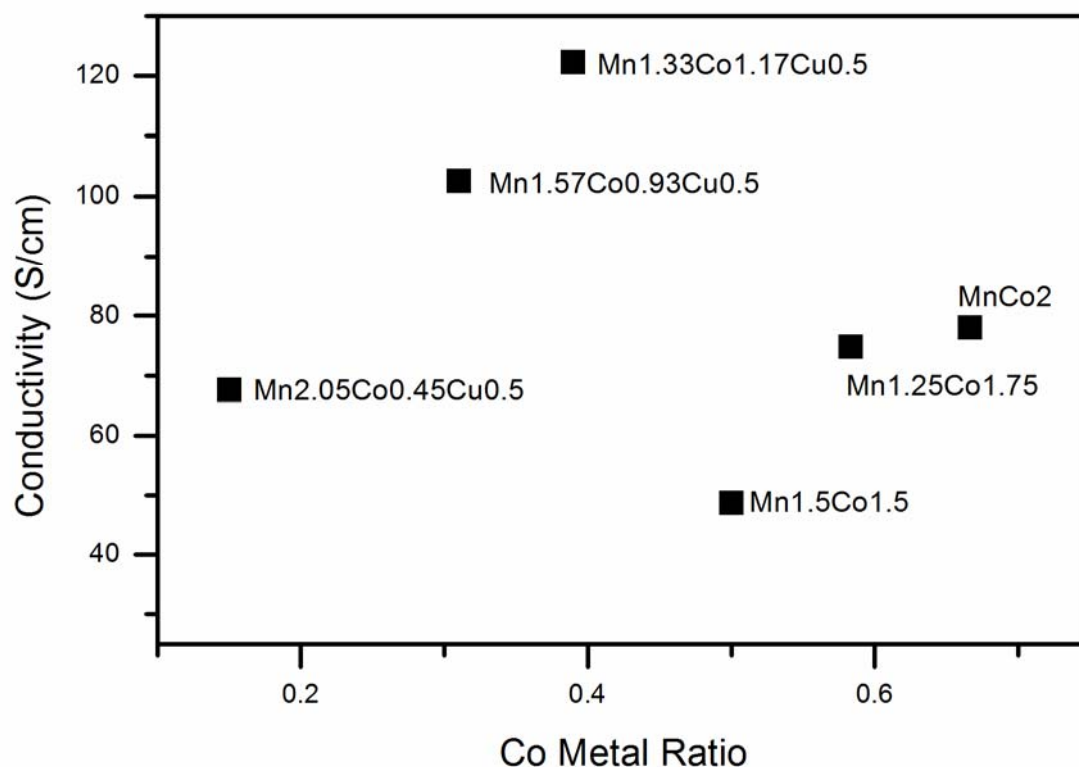
Sample	Temperature range	Ea (eV)
	(°C)	
MnCo₂	500-800	0.55±0.02
Mn_{1.25}Co_{1.75}	500-800	0.54±0.04

Mn1.5Co1.5	650-800	0.49 ± 0.02
Mn1.33Co1.17Cu0.5	500-800	0.34 ± 0.02
Mn1.57Co0.93Cu0.5	600-800	0.32 ± 0.03
Mn2.05Co0.45Cu0.5	750-800	0.32 ± 0.04



387

388 *Fig. 9: Arrhenius plots of electrical conductivity measured for the different samples.*



390

391 *Fig. 10. Conductivity values measured at 800°C as a function of the sample composition.*

392

393 4. Conclusions

394 Different Mn-Co and Cu-Mn-Co spinels were synthesised in order to evaluate the effect of Mn:Co
 395 ratio and copper addition on sintering behaviour, thermal expansion and electrical conductivity.

396 A High Energy Ball Milling treatment of oxide powders was utilized to produce highly reactive
 397 metastable multi-phase compounds that easily homogenize when brought to intermediate
 398 temperature ($T < 800^{\circ}\text{C}$) to form the equilibrium products. The influence of the different spinel
 399 compositions was observed on high temperature ($T > 1000^{\circ}\text{C}$) behaviour of each compound,
 400 evidencing that Cu decreases the spinel stability region. Thermogravimetric and in situ high
 401 temperature XRD analysis allowed to observe for the examined Cu-Mn-Co compositions a single
 402 cubic phase stable at high operating temperature (800°C). Different Mn:Co ratios did not lead to

403 significant differences in sintering behaviour, while Copper addition proved to be highly effective
404 in reducing sintering temperature and obtaining high densities.

405 Dilatometry experiments performed on sintered pellets allowed to observe a simple relation
406 between CTE and composition: CTE similarly increases with cobalt content, both in Mn-Co and
407 Cu-Mn-Co samples, with Cu doped samples characterized by higher CTE values.. A similar relation
408 could be observed also from electrical conductivity, being enhanced (up to 125S/cm) by Cu
409 addition and high cobalt content. The thermal expansion and electrical conductivity of Mn-Co
410 spinels can thus be tuned by varying stoichiometry.

411 Despite the best coating spinel composition cannot be given in absolute, because depending on the
412 interconnector alloy (and its CTE) and on the deposition process used, it is possible to state that the
413 fine tuning of stoichiometry is the strategy to design an ideal coating spinel. Cu addition to spinels
414 characterized by the opportune Mn-Co ratio represent a further possibility to optimize a material
415 capable to satisfy the properties required by the interconnect coating with the advantage of limiting
416 the use of an expensive and toxic element like Co.

417

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421

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